Taylor & Francis
Taylor & Francis Group

JOURNAL OF ENVIRONMENTAL ENGINEERING AND LANDSCAPE MANAGEMENT
ISSN 1648–6897 print/ISSN 1822-4199 online
2011 Volume 19(1): 34–43
doi:10.3846/16486897.2011.557473

ANTHROPOGENIC EFFECTS ON HEAVY METALS AND MACRONUTRIENTS ACCUMULATION IN SOIL AND WOOD OF *PINUS SYLVESTRIS* L.

Neringa Pundytė[1], Edita Baltrėnaitė[2], Paulo Pereira[3], Dainius Paliulis[4]

Dept of Environmental Protection, Vilnius Gediminas Technical University,
Saulėtekio al. 11, LT-10223 Vilnius, Lithuania
E-mails: [1]neringa.pundyte@vgtu.lt (corresponding author); [2]edita@vgtu.lt;
[3]pereiraub@gmail.com; [4]dainius@vgtu.lt

Submitted 13 Oct. 2010; accepted 23 Dec. 2010

Abstract. The investigation is focused on the uptake of heavy metals and macronutrients fluxes in *Pinus sylvestris* L. wood and soil under the sampled trees from contaminated and control sites. Soil pH, total organic carbon (TOC) and total and bioavailable heavy metals lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) and macronutrients, potassium (K) and magnesium (Mg) were compared on contaminated and control sites. Also, metal uptake of contaminated and control pine woods was determined. Concentrations of soil bioavailable Cd (0.009 mg kg^{-1}), Pb (0.11 mg kg^{-1}), Cu (0.076 mg kg^{-1}), Zn (0.51 mg kg^{-1}) and K (24.42 mg kg^{-1}), Mg (8.44 mg kg^{-1}) on the contaminated plot were significantly higher ($p < 0.001$) than on the control plot 0.00004 mg kg^{-1} for Cd, 0.007 mg kg^{-1} for Pb, 0.002 mg kg^{-1} for Cu, 0.22 mg kg^{-1} for Zn and 7.81 mg kg^{-1} for K, 2.40 mg kg^{-1} for Mg. In addition, the percentage of bioavailable metals in contaminated soils was higher. Pb (34.49 mg kg^{-1}), Cu (0.258 mg kg^{-1}), Zn (1.36 mg kg^{-1}) and K, Mg concentrations in wood were statistically higher than on the control site Pb (0.01 mg kg^{-1}), Cu (0.172 mg kg^{-1}), Zn (0.93 mg kg^{-1}), at $p < 0.05$ and $p < 0.001$, respectively. Cd did not show any significant difference in concentration on the contaminated plot in comparison to the control site.

Keywords: metal accumulation, soil contamination, heavy metals, macroelements, *Pinus sylvestris* L.

1. Introduction

Large amounts of chemical substances in the environment (air, soil and water) have an impact on humans and natural systems. Heavy metals in substantial amounts are important environmental pollutants and their toxicity is a problem for ecological, evolutionary, nutritional, and environmental reasons (Benavides *et al*. 2005). Heavy metals cause serious problems because of their easy spread and accumulation in soil and plants (Pantera *et al.* 2007; Stravinskienė 2005). Heavy metal pollution is related with the degree of industrialization and the intensity of chemical usage (Akinola *et at.* 2008) and is a serious problem for forest ecosystems (Stravinskienė ir Šimatonytė 2008; Nuhoglu 2005). However, plants have homeostatic cellular mechanism to regulate the concentration of metal ions inside the cell to minimize the potential damage from exposure to nonessential metal ions (Benavides *et al.* 2005).

Trees are considered sensors that record the environmental disturbances, as they live for a long time, stay in the same place all their lives and are widespread geographically. These factors make them especially suitable biological archives. Moreover, the observed effect of metal accumulation is a time-averaged result, which is more reliable than direct determination of the pollutant concentrations in air, for a short period (Kord *et al.* 2009). Coniferous species filter pollutant particles from the air (Salemaa 2003) capturing pollutants directly from the atmosphere, deposition on the needles or bark, or indirectly following deposition on the soil and subsequent root uptake (Nuhoglu 2006; Watmough 1999). Generally, conifers have much higher heavy metal content than deciduous species (Trüby 2005).

Determination of trees chemical composition is one of the most frequently used method to monitor environmental pollution (Ayodele and Ahmed 2001; Yilmaz and Zengin 2003). *Pinus sylvestris* L. is sensitive to environmental condition changes and takes up large amounts of pollutants and translocates them into the whole plant and can be considered as a proxy about the quality of the environment and thus is a good bioindicator (Rudovica *et al.* 2006; Mingorance *et al.* 2007). It is well known that changes of metal concentrations are related to the processes involving the uptake, transformation, storage and retranslocation of the elements. In *Pinus sylvestris* L., some metals are accumulated in roots, especially Pb, probably due to physiological barriers against metal transport to aerial parts, while others are easily transported in plants, for example, Cd (Boruvka *et al.* 1997; Kabata-Pendias and Pendias 2000). The uptake of heavy metals by *Pinus sylvestris* L. is a complex process and the uptake rate depends on soil pH, soil organic matter content and the concentration of other elements in soil (Baltrėnaitė and Butkus 2007; Seregin and Ivanov 2000). Depending on the element, tree species and availability of metal in the soil, the accumulation of metals varies (Trüby 2003). The main source of heavy metals entering the wood is related to the heavy metal uptake by roots from soils. On the root surface heavy metals bind to the carboxy-groups of mucilage uronic acids. The ability of mucilage to bind heavy metals decreases in the cation series: $Pb^{+2} > Cu^{+2} > Cd^{+2} > Zn^{+2}$. Furthermore, heavy metals enter the tree also from the atmosphere through the needles and bark with partial translocation into the wood (Scherbenko *et al.* 2008).

Data on the elemental composition of perennial plant organs, especially stem wood, are scarce and they are especially rare for forests under conditions of aerial pollution (Watmough and Hutchinson 1996; Saarela *et al.* 2005; Shcherbenko *et al.* 2008). The knowledge of the elemental content in the stem wood, needles and bark of *Pinus sylvestris* L. are of great environmental and industrial interest (Saarela *et al.* 2005), because it is a useful tool for analysing environmental changes and quantifying the impact of air pollution on forests (Ferretti *et al.* 2002).

The objectives of this study were to a) determine concentrations of heavy metals Pb, Cd, Cu, Zn and macronutrients K and Mg in the stand soil of *Pinus sylvestris* L. and to evaluate elements concentrations in the stemwood; b) to use Global analysis throughout principal component analysis (PCA) to identify relation among elements in soil, pinewood and soil properties and determine differences between sampling plots.

2. Materials and methods

Study site and sampling procedures

Two sampling plots (contaminated and control) located in Lithuania (Eastern Europe) were analysed in the study (Fig. 1). The first sampling plot (55⁰44´04´´N, 24⁰23´30´´E) is located in the city of Panevėžys near the former TV manufacturing company (Fig. 2). For more than 40 years, this factory has been manufacturing glass components, colour TV-tubes and electron-gun systems. It was the only manufacturer of TV tubes in the Baltic States since 1962 ("Ekranas" Company's Annual Report 2004). Total emissions from the manufacturer have been estimated 765.7 tonnes/ years. The emission levels have varied for total nitrogen oxides (NO_x) – 552.9 tonnes/ years, carbon monoxides (CO) – 154.8 tonnes/years, volatile organic compounds (VOCs) – 45.8 and 14.9 tonnes/years for particulate matter (PM). According, the Environmental Protection Agency (EPA), the manufacturer was one of the most polluting ones in 2004. Intensive contamination by heavy metals, Pb, Cd, Cu and Zn was caused by the manufacturer aerosol emission, significantly influencing the total soil geosanitary state. Heavy metals migrated in the soil horizons, consequently, high heavy metal and particularly Pb are dominant in the soil around the Company's sanitary zone (Strategic environmental assessment report of Panevežys city 2007).

The second sampling plot, the control one, (54⁰53´12´´N, 24⁰04´35´´E) is located near the city of Kaunas in the experimental forest of Dubrava Institute (Fig. 3). The control plot had a similar soil type and species as the contaminated plot, the sand and sandy loam soil type is prevailing on both plots. The control plot is outside the range of influence by nearby polluting sources, because it is in the outskirts of the city and is surrounded by a forest. The closest traffic road is 300 m away.

Sampling was carried out early in May 2009, during vegetation period when plants are most physiologically active (Hill 2002).

The contaminated plot was located at about 200 m from the Company. Southwest winds are reported to be dominant (Panevėžys city municipality 2005).

Sampled trees (*Pinus sylvestris* L.) were at least 10 m away from each other. Ten trees of a similar diameter were randomly selected in each control and contaminated plot. Tree cores were taken at breast height (1.5 m) from the north-facing side (facing the industry) (Watmough and Hutchinson 2005) using an acid washed 10 mm stainless steel increment borer. Samples were immediately sealed in dry, plastic straws and were stored for further analysis.

40 contaminated and 20 control soil samples from the north and south direction were collected near the selected trees from 0–20 cm soil profile and stored in plastic bags.

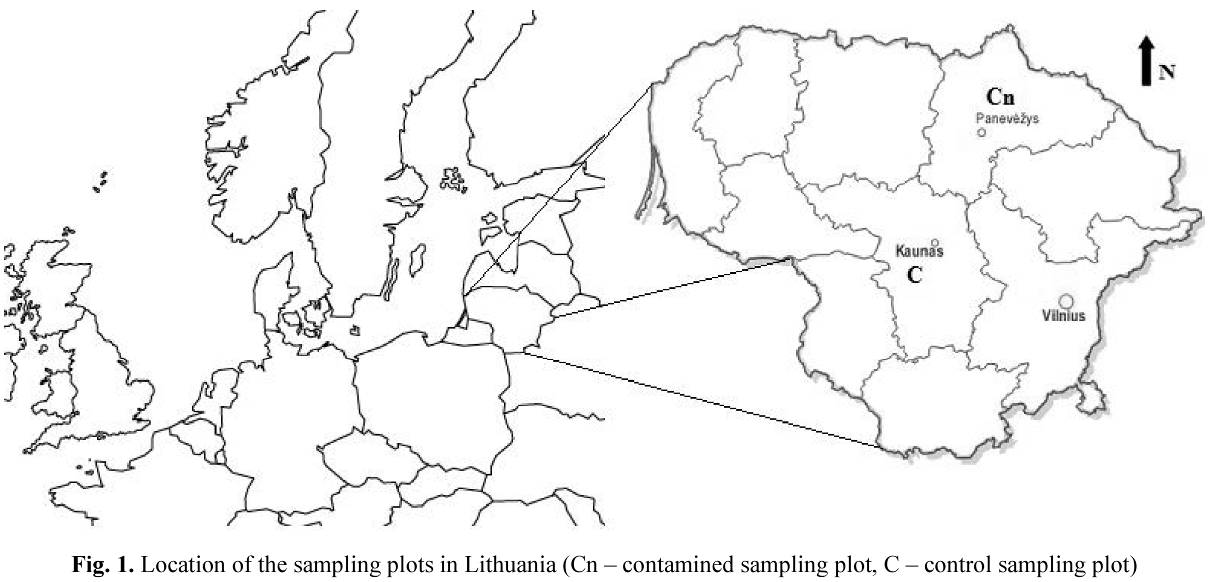


Fig. 1. Location of the sampling plots in Lithuania (Cn – contamined sampling plot, C – control sampling plot)

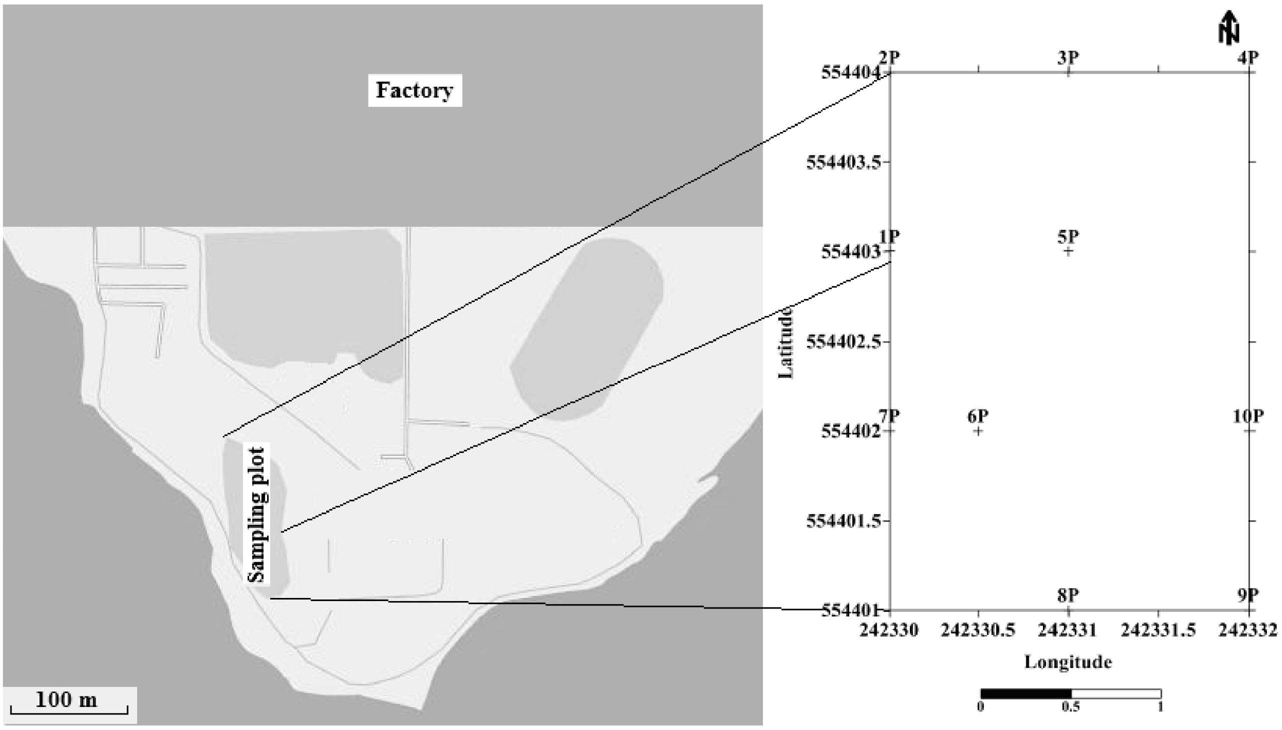


Fig. 2. Location of the contaminated study plot (55044´04´´N, 24023´30´´E). 1P, 2P, 3P etc. – trees sampled on the contaminated plot

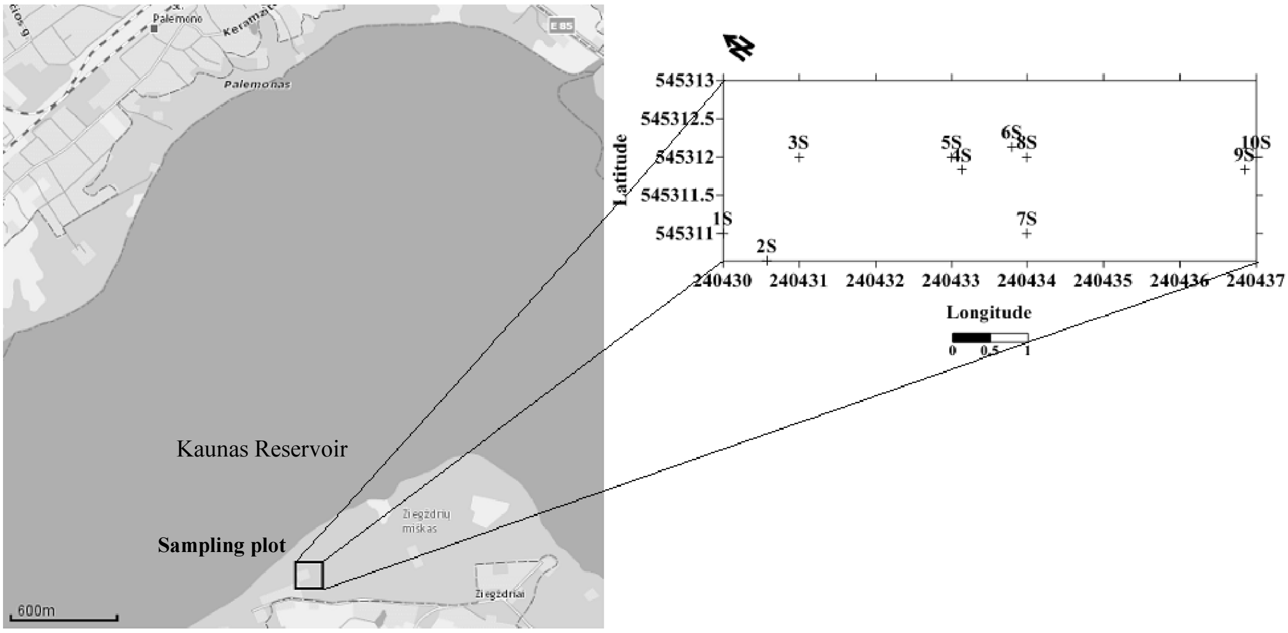


Fig. 3. Location of the control study plot ($54^0$53´12´´N, $24^0$04´35´´E). 1S, 2S, 3S etc. – trees sampled on the control plot

Soil pH

Soil pH was measured using a soil-water ratio 1:5 and a glass electrode pH meter *pH 538 WTV*. 20 g of the soil was mixed with 100 ml deionised water and was shaken for 1 hour using mechanical shaker *Gerhardt, Rotoshake RS 12*. The mixture was left for 60 minutes to allow it to settle. The electrode of pH meter was put into the slurry and measured 3 times in one solution.

Total organic carbon in soil

TOC was determined using apparatus TOC-V by SHIMADZU at 900 °C temperature. TOC content was recalculated using Eq. (1):

$$W_{C,t} = 1000 \times \frac{m_2}{m_1} \times 0.2727, \qquad (1)$$

where $W_{C,t}$ – TOC on basis of air-dried soil, g kg^{-1}; m_1 – mass (g) of test portion, g; m_2 – mass of released CO_2, g; 0.2727 – conversion factor for CO_2 to C (ISO 10694:1995).

Total elements in soil

Soil samples were air-dried at room temperature for 24 hours, sieved (2 mm mesh) and weighed 0.2 g, then mixed with 9 ml HCl (37%) and 3 ml HNO_3 (65%), poured into special vessels and then placed into a Milestone ETHOS digestor and heated for 30 min. The solution was then poured into 50 ml flask and diluted with distilled water to reach the marks of 50 ml (Butkus and Baltrėnaitė 2007; Baltrėnas *et al.* 2009).

The total concentrations of elements in soil and wood samples were determined by flame atomic absorption spectrophotometry (FAAS). A graphite furnace (GFAAS) was employed to determine metal concentrations when they were too low to be detected accurately by FAAS (Baltrėnaitė *et al.* 2010; Butkus and Baltrėnaitė 2007).

Bioavailable elements in soil

Bioavailable elements in soil were assessed by water extraction of 20 g soil in 100 ml of distilled deionised water. Soil-water samples were shaken in *Gerhardt, Rotoshake RS 12* for 1 hour and left to settle. Afterwards extracts were collected by filtration through filter paper and analysed for Pb, Cd, Zn, Cu, K, Mg concentrations by FAAS or GFAAS.

The ratio (%) of bioavailable elements in soil was calculated using Eq. (2):

$$C_{bioav,\%} = \frac{C_{bioav}}{C_{tot}} \cdot 100\% , \tag{2}$$

where $C_{bioav,\%}$ – the percent of bioavailable elements in soil C_{bioav} – mean bioavailable metal concentration in soil solution, mg kg^{-1}; C_{tot} – mean total metal concentration in soil, mg kg^{-1} DW.

Total elements in wood

Each core was burnt for 45 min in E5CK-T muffle furnace (450 °C) and weighted, then mixed with 9 ml HCl (37%) and 3 ml HNO_3 (65%), poured into mineralization vessels and the same methods, described in total elements in soil analysis, were used.

Data analysis

Some descriptive statistics were performed, average and standard deviation (SD) and statistical significance between elements concentrations between contaminated and control plot were assessed with a Student *t-test*. The differences were considered significant at $p < 0.05$.

A multivariant analysis of the results was made using principal component analysis (PCA), based on correlation matrix. The components of PCA were rotated by a varimax rotation. The aim of using PCA was to ascertain any patters in all the samples in relation to chemical characteristics and draw a preliminary conclusion about the possible relationship among metals in soil, wood and soil properties (Jia *et al.* 2010). This methodology was applied in order to identify relation between variables, differences between control and contaminated plots and potential detection of anthropogenic pollutants source (Li *et al.* 2009). All the calculations were performed using the statistical packages Statistica 6.0 (Statsoft.Inc).

3. Results and discussion

Total elements in soil

The values of soil pH, TOC, total and bioavailable elements in the control and contaminated soil plots are summarized in Table 1.

Table 1. Mean soil pH, TOC and total and bioavailable metals in control and contaminated soils. ± (Standard deviation) SD. Data in mg kg^{-1} DW in total elements

	Control soil (n = 20)	Contaminated soil (n = 40)	P
pH	5.29±0.09	6.59±0.06	***
TOC	2.47±0.48	4.22±0.34	***
Mg^{tot}	497±73	498±72	n.s
K^{tot}	1282±87	1107±62	n.s
Pb^{tot}	2.99±3.24	25.6±2.3	***
Cd^{tot}	0.719±0.19	0.278±0.13	n.s
Cu^{tot}	0.01±0.80	23.2±0.6	***
Zn^{tot}	40.5±5.5	36.9±3.6	n.s

n – number of soil samples; significant differences between plots: *** – $p < 0.001$; n.s. – non significant differences.

Soil has an ability to immobilise introduced heavy metals. According to Borůvka and Drábek; Toribio and Romanya; Dube *et al.* soil organic carbon together with soil pH is the most important parameter controlling heavy metal immobilisation in the soil. Soil pH was found to play the most important role in determining metal speciation, solubility of metals, due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution. A negative correlation between soil pH and heavy metal mobility and availability to trees has been well documented. For instance, decreased soil pH increases in heavy metal desorption from soil constituents and dissolution in soil solution were observed for Cd, Pb and Zn. The mobility and bioavailability of heavy metals also increase with decreased soil pH, thus enhancing the uptake of heavy metals by trees (Zeng *et al.* 2010).

The results of the studied soil pH varied from 5.69 to 7.78 and 4.62 to 6.04 on contaminated and control sites, respectively, indicating moderately acid to slightly alkaline soil on the contaminated site, strongly acid to moderately acid on the control plot. Soil pH influences macronutrients uptake and tree growth. Many soil macronutrients change the form because of reactions in the soil that are largely controlled by soil pH, consequently trees may not be able to use these changed macronutrients (Arduini *et al.* 1998). TOC ranged from 1.52 to 9.98 g kg^{-1} on the contaminated plot and from 0.39 to 9.86 g kg^{-1} on the control plot. The averages of soil pH and TOC at a depth of 0–20 cm of soil profile on contaminated and control plots are summarized in Table 1. Values of TOC and pH on the contaminated plot were statistically higher than on the control plot. Furthermore, average pH value of the contaminated plot approached to neutral (7.0) pH. The higher pH value can be a result of greater retention of metals and their lower solubility in the soil of the contaminated plot. Moreover, high soil pH can stabilize heavy metals, resulting in decreased leaching effects of the soils heavy metals, additionally heavy metals become stabilized due to high soil pH which may result in lower element concentration in the soil solution. This may restrain the absorbability of the elements from the soil solution and transportation into tree tissues (Malik *et al.* 2010).

Background and limit values of concentrations for heavy metals Pb, Cd, Cu and Zn in Lithuania are given in Table 2 (Hygiene Standard of Lithuania HN 60:2004). Although the manufacturing Company was closed (it went bankrupt in 2004) at the time of sampling and there were no emissions into the air, the concentrations for Cd, Zn and particularly Cu and Pb were higher than the background values on the contaminated plot, though limit values were not exceeded for all investigated heavy metals. The total concentrations of Pb and Cu (except Zn and Cd) under trees on the control plot were below their environmental background values, indicating that this area received minimal atmospheric heavy metals input (Kuang *et al.* 2007).

Table 2. Background and limit values of heavy metals for Lithuanian moderate sandy soil (Hygiene Standard of Lithuania HN 60:2004)

Metal	Background values, $mg \cdot kg^{-1}$	Limit values $mg \cdot kg^{-1}$
Pb	15	100
Cd	0.15	3
Cu	8.1	100
Zn	26	300

On the contaminated plot total heavy metal concentrations in the upper soil (0–20 cm) under the sampled trees ranged from 8.42–37.4 mg kg^{-1} for Pb; 0.167–0.483 mg kg^{-1} for Cd; 12.7–31.7 mg kg^{-1} for Cu; 18.5–115 mg kg^{-1} for Zn. Similarly, heavy metal concentrations were reported according to Watmough *et al.* (2005). On the control plot (0–20 cm) heavy metal concentrations ranged from 1.56–5.03 mg kg^{-1} for Pb; 0.02–5.16 mg kg^{-1} for Cd; 0.006–0.03 mg kg^{-1} for Cu; 22.5–96.5 mg kg^{-1} for Zn. Heavy metal concentrations on both studied plots confirm that the contaminated plot was affected by high heavy metal deposition (total Pb and Cu concentrations on the contaminated plot were statistically ($p < 0.001$) higher than those on the control plot) and present contamination and clear differences between plots by Pb and Cu.

Bioavailable metals

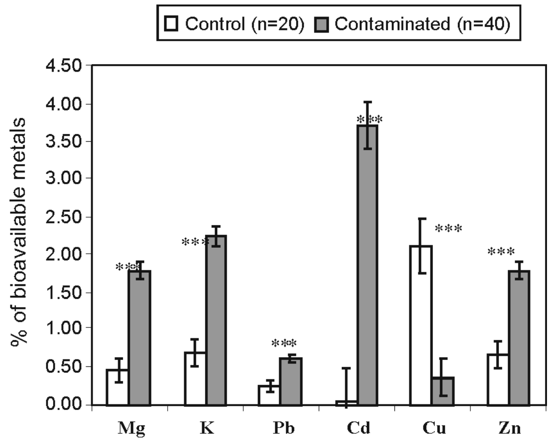
Results obtained in this work from analyses of bioavailable metals are listed in Table 3. The highest bioavailable concentrations were found for Zn on both sampling plots. For all the bioavailable metals, higher concentrations were found the contaminated plot than on the control plot and confirmed higher proportion of total metals that are available for trees.

The bioavailable concentrations are usually only 1–5% of the total concentrations (Tarvainen and Kallio 2002). Fig. 4 shows the percentage of bioavailable metals to total metals on control and contaminated plots.

Table 3. Bioavailable metals in control and contaminated soils. ± (Standard deviation) SD. Data in mg kg^{-1} DW in bioavailable concentrations

	Control soil (n = 20)	Contaminated soil (n = 40)	P
$Mg^{(b)}$	2.40±1.17	8.44±0.83	***
$K^{(b)}$	7.81±2.15	24.42±1.52	***
$Pb^{(b)}$	0.007±0.006	0.11±0.004	***
$Cd^{(b)}$	0.00004±0.001	0.009±0.0007	***
$Cu^{(b)}$	0.0002±0.007	0.076±0.005	***
$Zn^{(b)}$	0.22±0.03	0.51±0.02	***

n – number of soil samples; significant differences between plots: *** – $p < 0.001$.



n – number of soil samples; significant differences between plots: *** – $p < 0.001$.

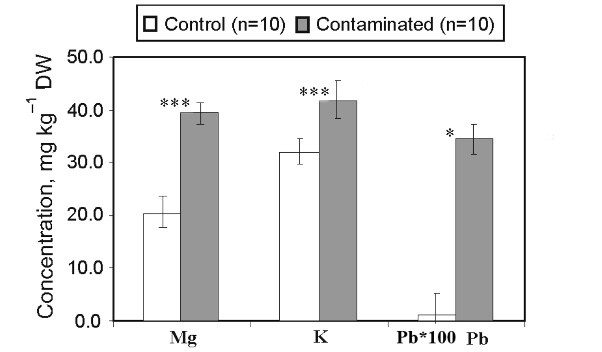
Fig. 4. Bioavailable metals in control and contaminated soils, %. Values are means±SD (vertical lines)

Percentage of bioavailable Pb, Cd, Zn, K and Mg (except Cu) on the contaminated plot was significantly higher ($p < 0.001$) than on the control plot. In neutral soil reaction (pH 7.0) bioavailability of Cu is very low (Mažvila 2001), as a result the contaminated plot pH (6.59) approximate to neutral thus having lower bioavailable metal concentration than in control soil where pH was more acidic. The results on the contaminated plot indicated higher bioavailability of metals, to be precise, higher amount of metals that are available for tree uptake.

Total elements in wood

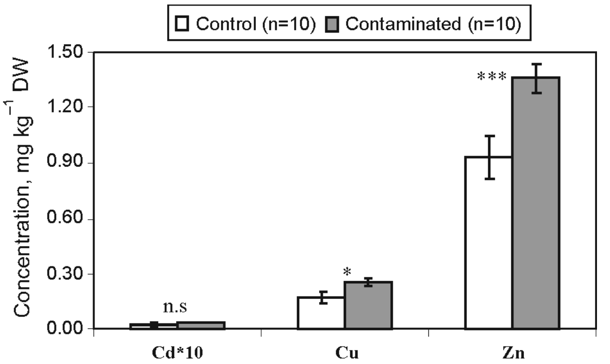
Heavy metals and macroelements taken by a pine tree were also accumulated in the stemwood. Elements concentrations in sampled pine stemwood on both contaminated and control plots are summarized in Figs 5 and 6.

Heavy metal concentration in wood decreased in the following order: Pb > Zn > Cu > Cd on the contaminated site and Zn > Cu > Pb > Cd in control site. The contaminated plot showed high Pb accumulation, although, Pb is rather immobile in soil and concentrates primarily in the roots and is poorly translocated to the tree parts, resulting in a comparatively low transfer factor from soil to a tree (Madejon *et al.* 2004). In general, Cd is absorbed by higher plant roots and accumulated in aboveground organs, having thus a comparatively high transfer soil-tree



n – number of wood samples; significant differences between plots: * – $p > 0.05$ and *** – $p < 0.001$.

Fig. 5. Concentration of Mg, K and Pb in wood on both control and contaminated plots. Values are means ±SD (vertical lines). Value of Pb concentration (control) is multiplied by 100



n – number of wood samples; significant differences between plots: * – $p > 0.05$ and *** – $p < 0.001$; n.s. – non significant differences.

Fig. 6. Concentration of Cd, Cu and Zn in wood on both control and contaminated plots. Values are means ±SD (vertical lines). Values of Cd concentration (control) is multiplied by 10

factor (Alloway 1995). Zn has relatively high transfer factor from soil to a tree and most plants can tolerate high Zn levels. Heavy metals such as Zn, Cd are readily translocated to the top of a tree, Cu is intermediate and Pb is translocated to the least extent (Alloway 1995). Pb, Cu and Zn, concentrations in pinewood on the contaminated site were significantly higher ($p < 0.05$ and $p < 0.001$) than those on the control plot.

According to Saarela *et al.*; Mingorance *et al.*, Pb concentrations in wood of pine tree were very low, for instance 0.1±0.07 mg kg^{-1} or 3.72±0.38 mg kg^{-1}. The average concentration of Pb in contaminated stemwood showed extremely high values comparing to a control sample, though, Pb is not an essential element (Seregin and Ivanov 2001), however, in our case it was easily absorbed and accumulated in stemwood. The mean Pb concentrations were 34.5 (±2.9) mg kg^{-1} on the contaminated plot and low concentration was 0.01 (±4.10) mg kg^{-1} on the control plot. Although Pb accumulation in the stemwood can be explained mostly by root uptake from soil, however, in our case, the soil concentration of Pb was only 25.6±2.3 mg kg^{-1}, therefore, bark uptake pathways could lead from atmospheric depositions from stack emissions, consequently influencing a higher Pb concentration in contaminated wood.

Cd tends to be very mobile in soil systems and therefore available to trees (Fritioff and Greger 2007). In most environmental conditions, Cd enters first the roots, and only small amounts are transported to the shoots, the content decreases in the order: roots>stems>seeds (Benavides *et al.* 2005), consequently Cd showed low concentrations in both plots. On the contaminated plot concentrations varied only 0.002–0.013 mg kg^{-1}, in the control plot 0.001–0.007 mg kg^{-1}.

In the study Cu concentrations were similar and varied 0.097–0.57 mg kg^{-1} and 0.07–0.65 mg kg^{-1} in the contaminated and control plots, respectively, however, no Cu contamination was found. Not only bioavailable Cu concentration can be taken by trees but also and the part of soil-immobilized Cu, because it's a necessary element for tree nutrition (Mažvila 2001).

Mean concentration of Zn in contaminated wood was 1.5 times higher than in control wood and varied from 0.775 to 2.182 mg kg^{-1}; from 0.47 to 1.64 mg kg^{-1}, respectively. It can be concluded that airborne heavy metal pollution leads to some degree of soil pollution but it is not easily reflected in stemwood data.

Other ions such as K^{+} and Mg^{+2} considerably affect the uptake of heavy metals by various plant tissues (Seregin and Ivanov 2001). However, pinewood is characterized by a lower contents of macroelements in comparison with the other organs (Shcherbenko *et al.* 2008). The concentration of two mineral elements K and Mg are lower in the samples from the control plot K – 22.9–55.5 mg kg^{-1}; Mg – 11.3–55.6 mg kg^{-1} than in contaminated plot K – 24.1–72.8 mg kg^{-1}; Mg – 30.5–65.8 mg kg^{-1}.

Global Analysis

Global analysis was carried out throughout a principal component analysis (PCA). This method is a useful tool in the examination of multivariant data (Topalian *et al.* 1999). The PCA applied in this study identifies five Factors that explained at least one variable and in total, explain 81.94% of the total variability: Factor 1 (47.42%), Factor 2 (14.06%), Factor 3 (11.43%), Factor 4 (4.69%) and Factor 5 (4.33%). The first two factors explained more than 60% of the total variance. Fig. 7 shows the relation between these two factors. In total we identified four groups: the first group composed for all the elements concentration in wood, total Zn and soil TOC, the second group – for total Mg, K and Cd%, the third group for total Cd, Pb% and Zn% and the fourth group for the remaining elements. From these results we can observe as expected that the majority of bioavailable elements on the control (Cn) and contaminated (C) plots depends on the pH values and the concentration of elements in wood is related with soil TOC. With the exception of Zn, Pb and Cd the percentage of elements in solution were strongly correlated with bioavailable elements (Fig. 7). The PCA also allows us to classify the differences between the control and contaminated plots. Thus we observed that the minor % of Cd extraction on the contaminated (Cn) plot in relation to the control (C) plot, decreased significantly. In relation to total concentration of K, Mg and Cd in wood no significant differences were founded. For the remaining elements the concentrations were significantly higher on the contaminated (Cn) plot. Fig. 8 represents the relation of Factor 1 and Factor 2 in consideration of all cases. The results showed that the concentration of the studied elements in contaminated (Cn) and control (C) plots is different and this suggests that some anthropogenic factor might be responsible for this difference, as observed in other studies (Li *et al*. 2009; Franco-Uría *et al.* 2009; Wu and Zhang 2010).

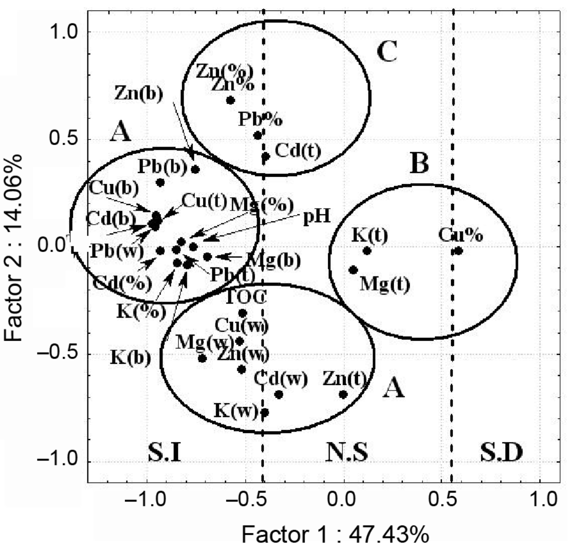


Fig. 7. Relation between Factor 1 and Factor 2 (Variables). A (first group, TOC, Cu(w), Mg(w), Zn(w), Cd(w), K(w) and Zn(t)), B (second group, Mg(t), K(t) and Cu%), C (third group, Zn%, Pb% and Cd(t)) and D (fourth group, Zn(b), Pb(b), Cu(b), Cu(t), Cd(b), Pb(w), Cd%, K%, Pb(t), Mg%, pH, K(b) and Mg(b)). SI (Significant differences between sites, major concentration in contaminated plot), N.S. (non-significant differences between plots) and S.D. (Significant differences between sites, major concentration in control plot

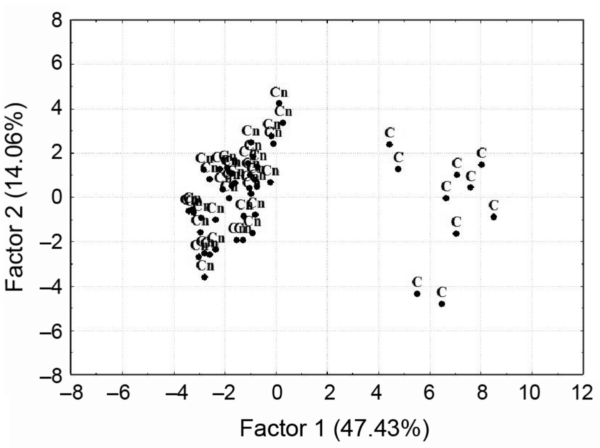


Fig. 8. Relation between Factor 1 and Factor 2 (Cases). Principal component plot of all the samples collected on contaminated (Cn) and control (C) plots

4. Conclusions

1. On the contaminated plot total Pb and Cu concentrations were statistically ($p < 0.001$) higher than those on the control plot. These higher contaminations are very likely to be due to the nearby factory. The concentrations for Cd, Zn and particularly Cu and Pb were higher than the background values on the contaminated plot, and this is a clear evidence of the manufacturer effects on the accumulation of these metals. Measures are needed to reduce the effects of this industry on the surrounding area. The total soil concentrations of Pb and Cu, except Zn and Cd on the control plot were below their environmental background values.

2. Average bioavailable concentrations of Pb, Cd, Cu, Zn, K and Mg on the contaminated plot were significantly ($p < 0.001$) higher than on contaminated. Thus, this indicates higher amount of heavy metals and macronutrients that are available for tree uptake on the contaminated plot. Moreover, total Cu concentration in contaminated soil due to high soil pH resulted in less concentration in the soil solution than on the control plot.

3. Average concentration of heavy metals Pb, Cu, Zn and macronutrients K and Mg in wood of the contaminated plot were statistically ($p < 0.05$ and $p < 0.001$) higher than on the control plot, therefore, demonstrated *Pinus sylvestris* L. wood as a biomonitor of heavy metals pollution.

4. The applied PCA allowed us to observe the relations between elements. The bioavailable elements are very dependent of pH, and metals concentration in *Pinus sylvestris* L. wood depends on soil TOC. The variability and concentration of metals between control (C) and contaminated (Cn) plot is very different, thus we can affirm that manufacturing emissions have an important effect on metals accumulation on soils and *Pinus sylvestris* L. wood.

Acknowledgement

We gratefully acknowledge the colleagues from the Department of Environmental Protection of Vilnius Gediminas Technical University for chemical analysis as well as Giedrė Raginytė and Laimonas Cvirka for assistance in the field and laboratory work.

Financial support from the Research Council of Lithuania (COST Action FA0905) is gratefully acknowledged.

References

Akinola, M. O.; Njoku, K. L.; Ekeifo, B. E. 2008. Determination of Lead, Cadmium and Chromium in the Tissue of an Economically Important Plant Grown Around a Textile Industry at Ibeshe, Ikorodu Area of Lagoa State, Nigeria, *Advances in Environmental Biology* 2(1): 25–30.

Alloway, B. J.; Ayres, D. C. 1997. *Chemical principles of environment pollution*. Second edition. London: Blackie Academic & Professional. 395 p.

Arduini, I.; Kettner, C.; Godbold, D. L.; Onnis, A.; Stefani, A. 1998. pH influence on root growth and nutrient uptake of *Pinus pinaster* seedlings, *Chemosphere* 36(4–5): 733–738. doi:10.1016/S0045-6535(97)10116-3

Ayodele, J. T.; Ahmed, A. 2001. Monitoring air pollution in Kano municipality by chemical analysis of Scots Pine (*Pinus sylvestris* L.) needles for sulphur content, *The Environmentalist* 21: 145–151. doi:10.1023/A:1010636528776

Baltrėnaitė, E.; Butkus, D. 2007. Modelling of Cu, Ni, Zn and Pb transport from soil to seedlings of coniferous and leafy trees, *Journal of Environmental Engineering and Landscape Management* 15(4): 200–207.

Baltrėnaitė, E.; Butkus, D. 2007. Transport of heavy metals from soil to *Pinus sylvestris* L. and Betula pendula trees, *Ekologija* 53(1): 29–36.

Baltrėnaitė, E.; Butkus, D.; Booth, C. A. 2010. Comparison of three tree – ring sampling methods for trace metal analysis, *Journal of Environmental Engineering and Landscape Management* 18(3): 170–178. doi:10.3846/jeelm.2010.20

Baltrėnas, P.; Vaitiekūnas, P.; Bačiulytė, Ž. 2009. Geležinkelio transporto taršos sunkiaisiais metalais dirvožemyje tyrimai ir įvertinimas, *Journal of Environmental Engineering and Landscape Management* 17(4): 244–251. doi:10.3846/1648-6897.2009.17.244-251

Benavides, M. P.; Gallego, S. M.; Tomaro, M. L. 2005. Cadmium toxicity in plants, *Braz. J. Plant Physiol.* 17(1): 21–34. doi:10.1590/S1677-04202005000100003

Borůvka, L.; Drábek, O. 2004. Heavy metal distribution between fractions of humic substances in heavily polluted soils, *Plant Soil Environ.* 50(8): 339–345.

Boruvka, L.; Kozak, J.; Krištoufkova, S. 1997. Heavy metal accumulation in plants grown in heavily polluted soils, *Folia Microbiol.* 42(5): 524–526. doi:10.1007/BF02826567

Butkus, D.; Baltrėnaitė, E. 2007. Accumulation of heavy metals in tree seedlings from soil amended with sewage sludge, *Ekologija* 53(4): 68–76.

Butkus, D.; Paliulis, D.; Baltrėnaitė, E. 2004. Sorption of heavy metals from polluted water and their migration in the system soil – tree, *Journal of Environmental Engineering and Landscape Management* 12(4): 120–125.

Ferretti, M.; Innes, J. L.; Jalkanen, R.; Saurer, M.; Schäffer, J.; Spiecker, H.; Wilpert, K. 2002. Air pollution and environmental chemistry – what role for tree ring studies?, *Dendrochronologia* 20: 159–174. doi:10.1078/1125-7865-00014

Franco-Uría, A.; López-Mateo, C.; Roca, E.; Fernández-Marcos, M. L. 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW of Spain, *Journal of Hazardous Materials* 165: 1008–1015. doi:10.1016/j.jhazmat.2008.10.118

Hill, L. J. 2002. Branching out into biogeochemical surveys: a guide to vegetation sampling, in Roach, I. C. (Ed.). *Regolith and Landscapes in Eastern Australia, CRC LEME, Perth*, 50–53.

HN 60:2004. Pavojingų cheminių medžiagų didžiausios leidžiamos koncentracijos dirvožemyje [Maximum permissible concentrations of hazardous chemical materials in soil], *Valstybės žinios* 41–1357.

ISO 10694:1995. Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis). International Organization for Standardization.

Jia, L.; Wang, W.; Li, Y.; Yang, L. 2010. Heavy metals in soil and crops of an intensively farmed area: a case study in Yucheng City, Shandong Province, China, *Int. J. Res. Public Health* 7: 395–412. doi:10.3390/ijerph7020395

Kabata-Pendias, A. 2000. *Trace Elements in Soils and Plants*. Published by CRC Press. 413 p. doi:10.1201/9781420039900

Kord, B.; Mataji, A.; Babaie, S. 2009. Pine (*Pinus Eldarica* Medw.) needless as indicator for heavy metlas polllution, *Int. J. Environment Sci. Tech.* 7(1): 79–84.

Kuang, Y. W.; Zhou, G. Y.; Wen, D. Z.; Liu, S. Z. 2007. Heavy metals in bark of *Pinus massoniana* (Lamb.) as an indicator of atmospheric deposition near a smeltery at Qujiang, China, *Env. Sci. Pollut. Res.* 14(4): 270–275. doi:10.1065/espr2006.09.344

Li, J.; He, M.; Han, W.; Gu, Y. 2009. Analysis and assessment on heavy metal sources in coastal soils developed from alluvial deposits using multivariate statistical methods, *Journal of Hazardous Materials* 164: 976–981. doi:10.1016/j.jhazmat.2008.08.112

MacDonald, J. D.; Hendershot, W. H. 2006. Modelling trace metal partitioning in forest floros of northern soils near metal smelters, *Environmental Pollution* 143: 228–240. doi:10.1016/j.envpol.2005.11.031

Malik, R. N.; Husain, S. Z.; Nazir, I. 2010. Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan, *Pak. J. Bot.* 42(1): 291–301.

Mažvila, J.; Vaičys, M.; Motuzas, A. 2001. *Lietuvos dirvožemių užterštumas sunkiaisiais metalais.* Vilnius: Lietuvos mokslas. 245 p.

Mingorance, M. D.; Valdes, B.; Rossini Oliva, S. 2007. Strategies of heavy metal uptake by plants growing under industrial emissions, *Environmental International* 33: 514–520. doi:10.1016/j.envint.2007.01.005

Nuhoglu, Y. 2006. A new approach to air pollution determination using annual rings: dendro-chemical elemental analysis of annual rings by SEM-EDS, *Polish Journal of Environmental Studies* 15(1): 111–119.

Pantera, A; Papadopoulos, A. M.; Orfanoudakis, M. 2007. Trace element accumulation in tree rings of *Pinus Halepensis* during the last 140 years, *Global NEST Journal* 9(3): 286–292.

Rudovica, V.; Katkevics, V.; Viksna, A. 2006. *Studies of lead and cadmium pollution level in pine seedlings. Macro and trace elements,* 23th workshop. Leipzig: Schubert-Verlag, 168–173.

Saarela, K. E.; Harju, L.; Rajander, J.; Lill, J. O.; Heselius, S. J.; Lindroos, A.; Mattsson, K. 2005. Elemental analyses of pine bark and wood in an environment study, *Science of the Total Environment* 343: 231–241. doi:10.1016/j.scitotenv.2004.09.043

Salemaa, M. 2003. *Response of the understorey vegetation of boreal forest to heavy metal loading*. University of Helsinki. Academic dissertation in Terrestrial Plant Ecology. 43 p.

Seregin, I. V.; Ivanov, V. B. 2001. Physiological aspects of cadmium and lead toxic effects on higher plants, *Russian Journal of Plant Physiology* 48(4): 523–544. doi:10.1023/A:1016719901147

Shcherbenko, T. A.; Koptsik G. N.; Groenenberg, B. J.; Lukina, N. V.; Livantsova, S. Yu. 2008. Uptake of nutrients and heavy metals by pine trees under atmospheric pollution, *Moscow University Soil Science Bulletin* 63(2): 51–59. doi:10.3103/S0147687408020026

Stravinskienė, V. 2005. *Bioindikaciniai aplinkos vertinimo metodai:* mokomoji knyga. Kaunas: VDU leidykla. 215 p.

Stravinskienė, V.; Šimatonytė, A. 2008. Dendrochronological research of Scots pine (*Pinus sylvestris* L.) growing in Vilnius and Kaunas forest parks, *Journal of Environmental Engineering and Landscape Management* 16(2): 57–64. doi:10.3846/1648-6897.2008.16.57-64

Topalian, M. L.; Castane, P. M.; Rovedatti, M. G.; Salibian, A. 1999. Principal component analysis of dissolved heavy metals in water of the Reconquista river (Buenos Aires, Argentina), *Bulletin of Environmental Contamination and Toxicology* 63(4): 484–490. doi:10.1007/s001289901006

Watmough, S. A.; Hutchinson, T. C. 1996. Analysis of tree rings using inductively coupled plasma mass spectrometry to record fluctuations in a metal pollution epizode, *Environmental Pollution* 93(1): 93–102. doi:10.1016/0269-7491(95)00107-7

Watmough, S. A.; Hutchinson, T. C. 2005. A comparison of temporal patterns in trace metal concentration in tree rings of four common European tree species adjacent to a Cu – Cd refinery, *Water, Air, and Soil Pollution* 146: 225–241. doi:10.1023/A:1023952417583

Watmough, S. A. 1999. Monitoring historical changes in soil and atmospheric trace metal levels by dendrochemical analysis, *Environmental Pollution* 106: 391–403. doi:10.1016/S0269-7491(99)00102-5

Wu, C.; Zhang, L. 2010. Heavy metal concentrations and their possible sources in paddy soils of a modern agricultural zone, southeasthern China, *Environmental Earth Sciences* 60: 45–56. doi:10.1007/s12665-009-0168-4

Yilmaz, S.; Zengin, M. 2003. Monitoring environmental pollution in Erzurum by chemical analysis of Scots pine (*Pinus sylvestris* L.) needles, *Environmental International* 29: 1041–1047. doi:10.1016/S0160-4120(03)00097-7

Zeng, F.; Ali, S.; Zhang, H.; Ouyang, Y.; Qiu, B.; Wu, F.; Zhang, G. 2010. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants, *Environmental Pollution* 159: 84–91. doi:10.1016/j.envpol.2010.09.019

ANTROPOGENINIO POVEIKIO ĮTAKA SUNKIŲJŲ METALŲ IR MAKROELEMENTŲ KAUPIMUISI DIRVOŽEMYJE IR PUŠIES (*PINUS SYLVESTRIS* L.) MEDIENOJE

N. Pundytė, E. Baltrėnaitė, P. Pereira, D. Paliulis

Santrauka

Pagrindinis tiriamojo darbo tikslas – nustatyti sunkiųjų metalų kiekį paprastosios pušies (*Pinus sylvestris* L.), augusios šalia buvusios *Ekrano* gamyklos Panevėžyje, medienoje bei palyginti su augusios kontrolinėje teritorijoje. Įvertinta ir palyginta abiejų teritorijų dirvožemis, nustatyta dirvožemio pH, bendrosios anglies kiekis (TOC), įvertintos suminė ir judriosios fazės sunkiųjų metalų – švino (Pb), kadmio (Cd), vario (Cu), cinko (Zn) bei makroelementų – kalio (K) ir magnio (Mg) koncentracijos. Nustatyta į pušų medieną užterštoje ir kontrolinėje teritorijose patekusių metalų kiekiai. Akivaizdu, kad judriosios fazės metalų koncentracijos užterštoje teritorijoje (Cd – 0,009 mg·kg^{-1}, Pb – 0,11 mg·kg^{-1}, Cu – 0,076 mg·kg^{-1}, Zn – 0,51 mg·kg^{-1} ir K – 24,42 mg·kg^{-1}, Mg – 8,44 mg·kg^{-1}) yra didesnės ($p < 0,001$) nei kontrolinėje (Cd – 0,000 04 mg·kg^{-1}, Pb – 0,007 mg·kg^{-1}, Cu – 0,000 2 mg·kg^{-1}, Zn – 0,22 mg·kg^{-1} ir K – 7,81 mg·kg^{-1}, Mg – 2,40 mg·kg^{-1}). Pb (34,5 mg·kg^{-1}), Cu (0,258 mg·kg^{-1}), Zn (1,36 mg·kg^{-1}) ir K bei Mg koncentracijos buvo statistiškai didesnės užterštoje teritorijoje ($p < 0,05$) augusios pušies medienoje nei kontrolinės ($p < 0,001$) – Pb – 0,01 mg kg^{-1}, Cu – 0,172 mg·kg^{-1}, Zn – 0,93 mg kg^{-1}. Cd koncentracija užterštoje teritorijoje augusios pušies medienoje nedaug skyrėsi nuo kontrolinės.

Reikšminiai žodžiai: metalų kaupimasis, dirvožemio užtarša, sunkieji metalai, makroelementai, *Pinus sylvestris* L.

ВЛИЯНИЕ АНТРОПОГЕННОГО ЗАГРЯЗНЕНИЯ ТЯЖЕЛЫМИ МЕТАЛЛАМИ И МАКРОЭЛЕМЕНТАМИ НА ПОЧВУ И СОСНУ ОБЫКНОВЕННУЮ (*PINUS SYLVESTRIS* L.)

Н. Пундите, Э. Балтренайте, П. Перейра, Д. Палюлис

Резюме

Главной целью научно-исследовательской работы было определить количество тяжелых металлов в древесине сосны обыкновенной (*Pinus sylvestris* L.) на территории бывшего завода «Экранас» в Паневежисе и сравнить его с данными контрольной территории. В исследовательской работе оценены и сравнены почвы обеих территорий, определен показатель pH почвы, общее количество углерода (ОКУ), оценены общие и растворимые концентрации тяжелых металлов свинца (Pb), кадмия (Cd), меди (Cu), цинка (Zn), концентрации макроэлементов калия (K) и магния (Mg). Также оценено попадание металлов в древесину сосны в загрязненной и контрольной зонах. Замечена тенденция: концентрация растворимых металлов Cd (0,009 мг·кг$^{-1}$), Pb (0,11 мг·кг$^{-1}$), Cu (0,076 мг·кг$^{-1}$), Zn (0,51 мг·кг$^{-1}$) и K (24,42 мг·кг$^{-1}$), Mg (8,44 мг·кг$^{-1}$) в загрязненной зоне выше ($p < 0.001$), чем в контрольной, соответственно Cd (0,00004 мг·кг$^{-1}$), Pb (0,007 мг·кг$^{-1}$), Cu (0,002 мг·кг$^{-1}$), Zn (0,22 мг·кг$^{-1}$) ir K (7,81 мг·кг$^{-1}$), Mg (2,40 мг·кг$^{-1}$). Концентрации Pb (34,49 мг·кг$^{-1}$), Cu (0,258 мг·кг$^{-1}$), Zn (1,36 мг·кг$^{-1}$), K и Mg в древесине были статистически выше на загрязненной территории ($p < 0,05$), чем на контрольной ($p < 0,001$) – Pb (0,01 мг·кг$^{-1}$), Cu (0,172 мг·кг$^{-1}$), Zn (0,93 мг·кг$^{-1}$). Концентрация Cd на загрязненной территории существенно не отличалась от концентрации на контрольной территории.

Ключевые слова: накопление металлов, загрязнение почв, тяжелые металлы, макроэлемеинты, *Pinus sylvestris* L.

Neringa PUNDYTĖ. PhD student (2010), Dept of Environmental Protection, Vilnius Gediminas Technical University (VGTU). Master of Science (VGTU, 2010), Bachelor of Science (environmental engineering) VGTU, 2008. Research interests: heavy metals in soil and plants, environmental protection.

Edita BALTRĖNAITĖ. Dr, Assoc. Prof., Dept of Environmental Protecion, Vilnius Gediminas Technical University (VGTU). She gained her Environmental Engineering and Landscape Management Ph.D in 2007 from Vilnius Gediminas Technical University (Lithuania). Publications: author/co-author of ~ 25 scientific papers. Research interests: metal uptake and translocation in higher plants, anthropogenic impact, soil contamination, environmental management.

Paulo PEREIRA. Dr, Assoc. Prof., Dept of Environmental Protection, Vilnius Gediminas Technical University (VGTU); lecturer of Mykolas Romeris University. PhD of the GRAM (Mediterranean Environment Research Group) of University of Barcelona. Membership: European Geosciences Union (EGU), World Association of Soil and Water Conservation (WASWC), Spanish Fire Network. Research interests: Fire effects on soil and water chemistry, heavy metals on soils and water, impacts of agriculture in soil erosion, climate change and behaviour of extremes and sustainable development.

Dainius PALIULIS. Dr, Assoc. Prof., Dept of Environmental Protection, Vilnius Gediminas Technical University (VGTU). Doctor of Technological Sciences (air–cleaning devices), VGTU, 2000. Master of Science, Vilnius University (VU), 1996. Publications: co-author of more than 15 research papers. Research interests: air pollution, chemical pollutants of the environment, environmental chemistry.